

(200)  
T67m  
no. 1012

Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR

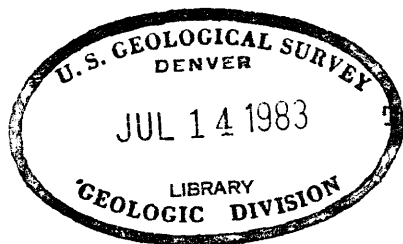
GEOLOGICAL SURVEY

PYRITE-URANINITE POLYCRYSTAL\*

By

A. G. King

August 1956



Trace Elements Memorandum Report 1012

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

\*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

## USGS - TEM-1012

## GEOLOGY AND MINERALOGY

<u>Distribution</u>	<u>No. of copies</u>
Atomic Energy Commission, Washington .....	2
Division of Raw Materials, Albuquerque .....	1
Division of Raw Materials, Austin .....	1
Division of Raw Materials, Casper .....	1
Division of Raw Materials, Denver .....	1
Division of Raw Materials, Ishpeming .....	1
Division of Raw Materials, Phoenix .....	1
Division of Raw Materials, Rapid City .....	1
Division of Raw Materials, Salt Lake City .....	1
Division of Raw Materials, Spokane .....	1
Division of Raw Materials, Washington .....	3
Exploration Division, Grand Junction Operations Office .....	1
Grand Junction Operations Office .....	1
Technical Information Service Extension, Oak Ridge .....	6
U. S. Geological Survey:	
Fuels Branch, Washington .....	1
Geochemistry and Petrology Branch, Washington .....	20
Geophysics Branch, Washington .....	1
Mineral Deposits Branch, Washington .....	1
P. C. Bateman, Menlo Park .....	1
A. L. Brokaw, Grand Junction .....	1
N. M. Denson, Denver .....	1
V. L. Freeman, College .....	1
R. L. Griggs, Albuquerque .....	1
W. R. Keefer, Laramie .....	1
M. R. Klepper, Spokane .....	1
P. K. Sims, Denver .....	1
L. R. Page, Washington .....	1
Q. D. Singewald, Beltsville .....	1
A. E. Weissenborn, Spokane .....	1
TEPCO, Denver .....	2
TEPCO, RPS, Washington, (including master) .....	2

## CONTENTS

	Page
Abstract .....	4
Introduction .....	4
Single-phase zoning .....	5
Two-phase zoning .....	7
Summary .....	13
References .....	13

## ILLUSTRATIONS

	Page
Figure 1. Uraninite ring textures .....	15
2. Single-phase zoning in pyrite .....	15
3. Two-phase zoning in pyrite .....	15
4. Zoned pyrite crystal with alpha tracks .....	8
5. Zoned pyrite crystal with systematic angular offset.	16
6. Two-phase zoning in pyrite .....	16

## PYRITE-URANINITE POLYCRYSTAL

By A. G. King

## ABSTRACT

A texture was observed in a sample of ore in which pyrite and uraninite occurred as thin alternate layers paralleling crystal faces of a pyrite nucleus. This texture could be formed either by replacement or by syntaxis. Although syntactic growth forming polycrystals of two chemically dissimilar minerals has not been previously described, this explanation fits the observed data better than the explanation offered by replacement. It is proposed, therefore, that this occurrence is an example of a polycrystal of uraninite and pyrite and that the mechanism of formation is syntaxis.

## INTRODUCTION

Growth-zoning phenomena in minerals are fairly common, and many authors have published descriptions of zoning in a wide variety of materials, including pyrite. The zoning has been shown by a color change between successive layers due to compositional differences or by symmetrically arranged inclusions.

A third type of growth zoning--two-phase zoning--is described in the following pages. This zoning is observed in a sample, collected by Art Baker, Vulcan Silver and Lead Co., and submitted to the Geological Survey for analysis by the U. S. Atomic Energy Commission. The sample is a highly mineralized siliceous boulder which was found in a stream

bed about 4 miles ENE of Marshall Pass, Saguache County, Colo. The rock contains pyrite, uraninite, quartz, and sphalerite (?) as primary minerals; and hematite, limonitic material, secondary uranium minerals, and quartz as alteration products and later introductions. An estimated 80 percent of the pyrite in the sample does not show zoning. Of the remaining 20 percent, about 19 percent is single-phase zoned and 1 percent two-phase zoned. The zoned pyrite occurs only in certain areas of the sample studied. The occurrence and distribution of the three types of pyrite suggest that there were at least two, and possibly three, different introductions of pyrite. As the three types of pyrite are spatially separated in the sections studied, it was not possible to establish the paragenesis.

Most of the uraninite is present in ring-shaped botryoidal textures surrounded and partly replaced by secondary uranium minerals and quartz (fig. 1). Some uraninite occurs as small irregular blebs dispersed in the gangue and as an irregular peripheral replacement of pyrite.

This short study is an outgrowth of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

#### SINGLE-PHASE ZONING

This type of zoning in the pyrite appears as layers that are made visible in polished sections owing to relatively slight differences in color. The colors range from light brassy yellow to a pale pinkish lavender. In a few crystals the dark colored layers are a light gray-lavender.

The two large crystals (fig. 2) measure about 50 microns in diameter, with the dark zones being from 2 to 3 microns thick. The dark banding is not uniform in color across the width of a layer but contains subtle variations in shading. The color at any one layer is probably related to composition, darker colors indicating greater amounts of atoms other than iron and sulfur.

The maximum color contrast between these layers and normal pyrite is shown in the large central crystal of figure 2. Various authors have published descriptions of similar material (Edwards, 1954; Ramdohr, 1950), and this occurrence is not considered unique. It is included as evidence that this single-phase growth zoning seems to be a separate phenomenon from the two-phase zoning described in the following pages.

The presence of a compositional difference might affect the pyrite unit-cell dimension. A few pyrite grains were handpicked from the sample and were analyzed by X-ray diffraction--using powder technique and manganese-filtered iron radiation. It was not possible to determine whether the grains analyzed were the zoned crystals or the more common unzoned pyrite. The small size of the pyrite crystals precluded separation of the three types of pyrite for more detailed investigation. The resultant diffraction pattern matched our pyrite standard except that the lattice was slightly expanded. The unit-cell dimensions were calculated by the method of Bradley and Jay (1932).

The pyrite has a unit-cell dimension of  $5.4275 \pm 0.001$  Å. Normally pyrite has a unit-cell dimension of 5.405 Å (Palache et al., 1946).

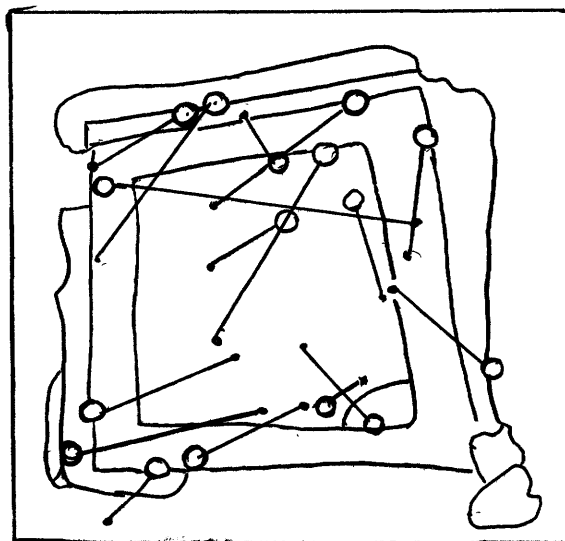
An attempt was made to separate a pure pyrite fraction for analysis, to determine the amount and kind of trace elements present. A pulp was separated by heavy liquids (methylene iodide) and then by differential chemical leaching (20 percent  $H_2SO_4$  on a steam bath for two hours). No pyrite was recovered.

#### TWO-PHASE ZONING

A few of the pyrite crystals have zoning that seems to be different from the color zoning described in the preceding pages (fig. 3). The dark zones are thinner, with sharper edges, and are composed of a material that in polished section is dark gray. The color contrast between this type of zone and the pyrite is much greater than that between the most intense individual color zones noted in pyrite (fig. 2). In the polished surfaces studied, no crystal was found to exhibit both types of zoning, and it is assumed that they occur independently of each other. The interfaces between some of these zones and the pyrite have a small amount of relief. This was interpreted as evidence for a slight difference of hardness between the pyrite and the gray zones.

A thinned polished section of this material was coated with a nuclear track emulsion (nuclear track emulsion in gel form, type C.2, Ilford Ltd., London), and a six-day exposure was made. The resultant alpha-track pattern in the emulsion indicated that these zoned crystals are radioactive. A camera lucida tracing was made of a zoned crystal and

its alpha-track pattern (fig. 4). The lines within the crystal and paralleling the faces show the position of the dark-gray zones. Because of the necessary magnification and the presence of an emulsion, it was not possible to draw the dark zones with their true width. The center of each zone is indicated by the lines. The dark zones in this particular sample are from about 0.25 to 0.5 micron in width. The open circles at one end of the projected alpha tracks indicate the point of emergence of the alpha particle from the polished surface.



0 5 10 microns

Figure 4.--Zoned pyrite crystal with alpha tracks.



Only those tracks were plotted that either showed both ends or whose ends could be inferred. More than half of the tracks shown are actual plots. The points of origin of the remaining tracks were inferred by extending the trajectory of the tracks to the polished surface as the microscope focus was lowered. At this magnification the inferred origin of the track is within about 0.5 micron of its true position. This particular nuclear track emulsion is in direct contact with the polished surface, whereas with stripping films it is separated by a cellulose ester backing. The projection in these circumstances does not have as great an error in the contact emulsion as it does in stripping film. Alpha tracks can be seen to originate from the dark-gray zones, showing that the zones are radioactive. Considering the width of the zones in this crystal, the length of exposure, and the fact that more than half of the tracks could not be plotted, the zones are at least moderately radioactive.

The mineral that comprises the dark-colored zones in the pyrite crystals is tentatively identified as uraninite. It is radioactive, has the color of uraninite in polished section, and is slightly softer than the pyrite. Most of the evidence is indirect, and there is some possibility of error. Because of the extremely small size of these crystals, and structural similarities between uraninite and pyrite, more direct methods of identification failed.

If we assume that this identification is correct, a very interesting hypothesis can be derived concerning the origin of this zoning.

The zoning in the color bands is rather obviously a crystal growth phenomenon. The composition, temperature, or pressure of the ore solution was rhythmically fluctuating as these crystals were deposited. One zoned pyrite crystal shows what may be a systematic offset of the crystallographic directions as the deposition progressed (fig. 5).

The rest of the zoning is much more regular, and the axes of the seed crystal are faithfully paralleled in subsequent layers.

One possible explanation of the zoning between pyrite and uraninite (?) is replacement. Compositional differences between color zones in pyrite might have permitted selective replacement by uraninite. A significant difference in solubility would be expected and might be magnified by galvanic action.

This explanation has a number of shortcomings. It is doubtful that a replacement of this sort would be so highly selective as to produce the sharp contacts between zones that are present. Few veinlets are seen connecting successive zones that would permit an exchange of material (fig. 3). No gradation is present between color zoning and two-phase zoning; either one or the other is present in a single crystal, but not both. There is also a difference in size of the two types of zoned pyrite crystals, the color-zoned crystals being larger by a factor of at least two and more usually about four. The dark zones in the single-phase crystals are about 2 to 3 microns in width, whereas the dark zones in the two-phase crystals are 0.25 to 0.5 micron in width. The variation in size and width of zoning suggests that these two types of crystals formed under different conditions and possibly at different times. If

replacement processes produced the two-phase zoning, we would expect the interfaces to be more irregular, more interconnecting veinlets to be present, the two types of crystals to have the same size distribution, and at least a few crystals with the zones partly replaced by uraninite (?). As such is not the case, this explanation was questioned.

An alternate explanation is offered. The literature cites numerous examples of crystals (Buckley, 1951), both natural and artificial, that are composed of one mineral containing oriented inclusions of another. A growing crystal face attracts atoms or structural fragments from the solution in which the crystal is growing. As these forces originate from atoms arranged in a lattice, the bounding forces also extend into the solution as an orderly array. An atom or structural fragment that is attracted to the crystal will, under ideal conditions, position itself so as best to satisfy the magnitude, "sign," and arrangement of these forces. This can result in the inclusion's growing crystallographically oriented with respect to the host.

By careful control of crystal-growth conditions it might be possible to form a continuous shell of the inclusion mineral which could completely encase the host mineral.

The term polycrystal was coined by G. Donnay (1953) to describe the syntaxic intergrowth of two distinct species. These polycrystals have been reported (G. Donnay and J. D. H. Donnay, 1953) forming from the species bastnaesite,  $\text{CeFCO}_3$ ; parisite,  $2\text{CeFCO}_3 \cdot \text{CaCO}_3$ ; roentgenite,  $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$ ; and synchisite,  $\text{CeFCO}_3 \cdot \text{CaCO}_3$ . If growth conditions reversed rhythmically so as to favor alternate deposition of the host and inclusion, it would be possible to build up parallel shells of the two minerals. This would

not be likely to occur if the two minerals were of dissimilar structures. We are concerned here with uraninite (?) and pyrite. Both minerals are isometric. Uraninite has variable unit-cell dimension of about 5.47 Å. The unit-cell dimension of the pyrite in this sample measured 5.4275 ± 0.001 Å. Uraninite is face-centered hexoctahedral. Pyrite is diploidal, with the iron atoms arranged in the sites of a face-centered lattice. The sulfur atoms are arranged in dumbbell-shaped pairs in the lattice and thus lower the symmetry displayed by the iron atoms alone. When these two unit cells are fitted together, the uranium and iron match atom to atom and the continuity of the face-centered lattice is preserved through both minerals. The sulfur atoms fit (or partly fit) in the depressions in the uraninite cell face between uranium atoms. Because of the structural similarities between these two minerals, it may be possible for them to fit together in this manner.

The large central zoned crystal in figure 6 started as euhedral pyrite. When the nature of the ore fluid or physical environment changed to favor the deposition of uraninite (?), a thin layer of this mineral was deposited on the surface of the crystal. If this layer were not crystallographically oriented with the pyrite, the next and successive layers of pyrite could not have nucleated with the same orientation as the first. If this is the case, then this occurrence is an example of a polycrystal between two compounds, very dissimilar chemically.

A similar type of zoning as that described here has been found on the Colorado Plateau in the Mi Vida mine (Weeks and others, 1956), and the Happy Jack mine (Trites and others, 1955).

## SUMMARY

The concept of polycrystals offers an alternate explanation to certain ore textures that in the past have been attributed to replacement processes. It may be possible to explain these textures more satisfactorily by crystal-growth phenomena, the explanation in certain instances being simpler and more direct than that offered by replacement.

The evidence presented here is largely inferential. Many of the uncertainties can be more satisfactorily answered when larger crystals exhibiting the same textures are found. Such materials could be analyzed by precession photographs, and if the two phases have the same crystallographic orientation, this evidence would be considered definitive.

The development of polycrystals may offer a satisfactory explanation of this two-phase zoning. In the material studied, this process is thought to offer a better explanation of the textures observed than a process involving replacement.

## REFERENCES

- Bradley, A. J., and Jay, A. H., 1932, A method for deducing accurate values of the lattice spacing from X-ray powder photography taken by the Debye-Scherrer method: *Phys. Soc. Proc.*, v. 44.
- Buckley, H. E., 1951, *Crystal growth*, New York, John Wiley and Sons.
- Donnay, Gabrielle, 1953, The "polycrystal," a product of syntaxic intergrowth (abs.): *Am. Crystallographic Assoc. meeting*, Ann Arbor, Michigan, June 22-26, 1953.
- Donnay, Gabrielle, and Donnay, J. D. H., 1953, The crystallography of bastnaesite, parisite, roentgenite, and synchisite: *Am. Mineralogist*, v. 38, p. 932-963.

- Edwards, A. B., 1954, Textures of the ore minerals and their significance, 2d ed., Melbourne, Australasian Inst. Mining Met.
- Palache, C., Berman, H., Frondel, C., 1946, Dana's system of mineralogy, 7th ed., New York, John Wiley and Sons.
- Ramdohr, Paul, 1950, Die Erzminerale und ihre Verwachsungen, Berlin, Akad. Verlag, 826 p.
- Trites, A. F., Jr., Chew, R. T., III, and Lovering, T. G., 1955, Mineralogy of the uranium deposit at the Happy Jack mine, White Canyon district, San Juan County, Utah: U. S. Geol. Survey Trace Elements Inv. Rept. 514.
- Weeks, A. D., Coleman, R. G., and Thompson, M. E., 1956, Summary of the mineralogy of the Colorado Plateau uranium ores: U. S. Geol. Survey Trace Elements Inv. Rept. 583.

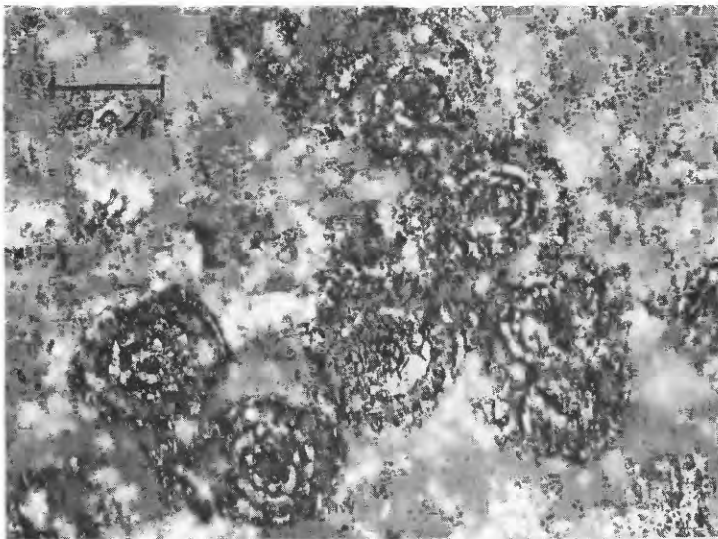


Figure 1.--Uraninite ring textures.

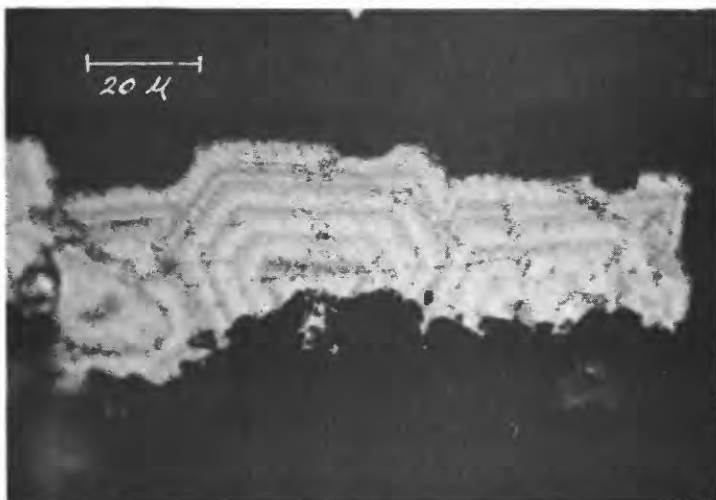


Figure 2.--Single-phase zoning in pyrite.

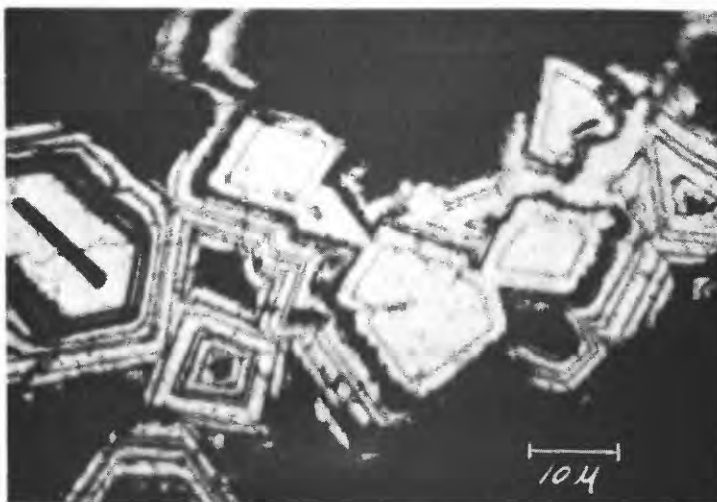


Figure 3.--Two-phase zoning in pyrite.

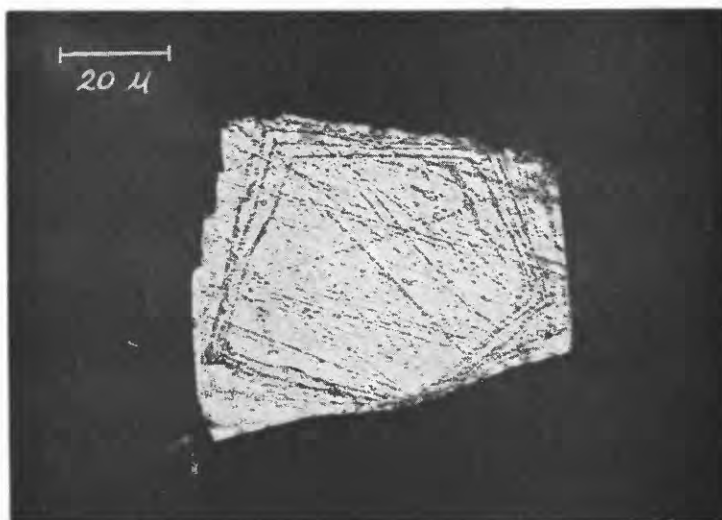


Figure 5.--Zoned pyrite crystal with systematic angular offset.

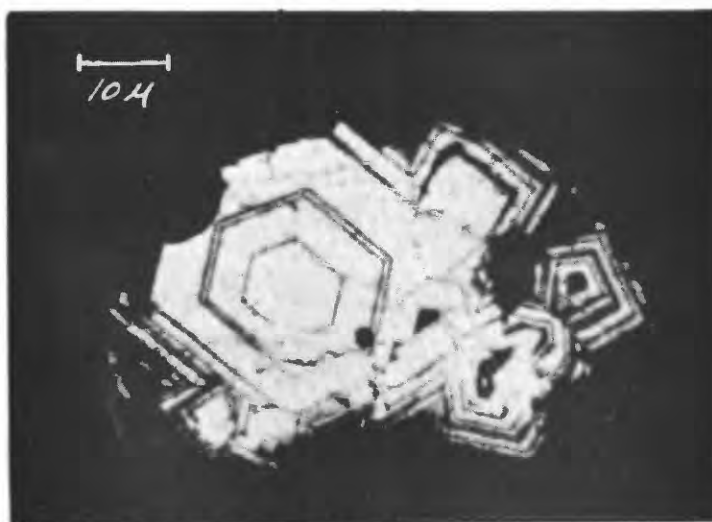


Figure 6.--Two-phase zoning in pyrite.